Effects of high hydrostatic pressure on rheological and thermal properties of chickpea (*Cicer arietinum* L.) flour slurry and heat-induced paste

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Running title
High pressure effect on chickpea flour slurry

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ABSTRACT

Thermorheological changes in high hydrostatic pressure (HHP)-treated chickpea flour (CF) slurries were studied as a function of pressure level (0.1, 150, 300, 400, and 600 MPa) and slurry concentration (1:5, 1:4, 1:3, and 1:2 flour-to-water ratios). HHP-treated slurries were subsequently analyzed for changes in properties produced by heating, under both isothermal and non-isothermal processes. Elasticity (*G*') of pressurized slurry increased with pressure applied and concentration. Conversely, heat-induced CF paste gradually transformed from solid-like behavior to liquid-like behavior as a function of moisture content and pressure level. The *G*' and enthalpy of the CF paste decreased with increasing pressure level in proportion with the extent of HHP-induced starch gelatinization. At 25 °C and 15 min, HHP treatment at 450 and 600 MPa was sufficient to complete gelatinization of CF slurry at the lowest concentration (1:5), while more concentrated slurries would require higher pressures and temperature during treatment or longer holding times.

Keywords: Chickpea flour; High pressure treatment; Oscillation test; Pasting; Gelatinization; Thermal properties

1. Introduction

Chickpea (*Cicer arietinum* L.) is a legume that is very commonly used in many countries because of its ideal cell wall polysaccharide composition and starch properties (Aguilera, Esteban, Benítez, Mollá, & Martín-Cabrejas, 2009). Foods based on this legume are prepared using a wide range of recipes and preparation procedures, among which heat processing is a well-established method. CF dispersion can form a gel under suitable processing conditions, and the gelling ability of chickpea flour/starch as well as the viscous nature of the cooked paste would be important for the manufacture and development of chickpea-based food gels. In starch-containing foods, the structure of a gel/paste is dictated by several factors (Kapri & Bhattacharya, 2008). These are: starch concentration, quantity of leached-out material, configuration of the swollen starch granule, amounts and types of amylose and amylopectin, and their interactions. The heating conditions, such as temperature, heating period. and rate of heating, are also equally important.

Therefore, improved use of chickpea can be obtained by implementing various processing strategies to facilitate development of easily manageable alternative products with optimized sensory qualities. In order to find ideal processing characteristics, two or more processing methods are commonly applied simultaneously (Wilson, Dabrowski, Stringer, Moezelaar, & Bocklehurst, 2008). One of the emerging technologies showing great potential for preserving plant-based food quality is HHP processing (Sila et al., 2008). HHP has been considered as being either alternative or complementary to thermal processing; the sensory properties of many HHP-treated fruit and vegetable products are superior to those of products preserved in the traditional way by heat treatment, although the process causes changes in texture (Ahmed, Ramaswamy, & Hiremath, 2005). Furthermore, HHP technology provides the possibility of producing foods with novel textures (Stolt, Oinonen, & Autio, 2001).

HHP treatment can also affect rheological properties of food products such as crushed fruits and vegetables, purée, pulp, and juice (Oey, Lille, Van Loey, & Hendrickx, 2008). The effects observed are dependent on HHP process conditions and type of fruit or vegetable. It has been shown that pressure-induced starch gelatinization is highly sensitive to changes in temperature, pressure, and treatment time (Bauer & Knorr, 2005). Ahmed et al. (2005) reported that the viscosity of mango pulp increased after HHP treatments at 100 or 200 MPa (20 °C/15 or 30 min), while a reduction in viscosity was observed after HHP treatments at 300 and 400 MPa (20 °C/15 or 30 min). The effect of HHP on the rheological properties of *Aloe vera* suspension was dependent on the pressure–time treatment (Opazo-Navarrete, Tabilo-Munizaga, Vega-Gálvez, Miranda, & Pérez-Won, 2012). HHP

94 treatment from 500 to 700 MPa for 1 and 2 min at 20 °C resulted in a significant increase in the viscosity of
95 tomato puree during chilled storage (Krebbers, Matser, Hoogerwerf, Moezelaar, Tomassen, & van den Berg,
96 2003). Likewise, it was reported that HHP pressure technology may offer new possibilities for starch-containing
97 foods, where an understanding of HHP-induced gelatinization of starch is vital for such applications (Vallons &
98 Arendt, 2009a, b). Several studies have investigated the effects of HHP on pure starch (Katopo, Song, & Jane,
99 2002) and on starch-in-water suspensions (Bauer & Knorr, 2005; Oh, Pinder, Hemar, Anema, & Wong, 2008a;
100 Oh, Hemar, Anema, Wong, & Pinder, 2008b; Vallons & Arendt, 2009a, b). However, little information is
101 available concerning the impact of HHP on whole flour systems. Ahmed, Ramaswamy, Ayad, Alli, & Alvarez
102 (2007) studied the effect of HHP treatment of basmati rice flour slurries and found gelatinization of starch and
103 denaturation of proteins. Ahmed, Varshney & Ramaswamy (2009) studied the thermal characteristics of HHP-
104 treated lentil flour slurries at selected moisture levels and found no starch gelatinization peak during thermal
105 scanning. It was also assumed that gluten inhibited HHP-induced starch gelatinization, explaining the lower
106 paste consistency of the wheat flour suspensions compared with the isolated starch (Vallons, Ryan, Koechler, &
107 Arendt, 2010).
108 To the best of our knowledge, no research has been performed on the effect of HHP on the rheological
109 properties of CF slurry. As the rheological properties of CF will affect the texture and sensory properties of
110 foods containing chickpea, an understanding of HHP-induced gelatinization of starch is vital for the development
111 of new chickpea applications using HHP. Knowledge of the fundamental rheological properties of any food can
112 be an indication of how the food will behave under various processing conditions (Ahmed et al., 2005).
113 Published data on the rheology of chickpea flour dough are scarce, and further studies would be of interest,
114 particularly on the oscillatory rheological characteristics.
115 The objective of this work was to evaluate the effect of HHP treatment on rheological and thermal
116 properties of CF slurry and to understand the pressure susceptibility of one of the major chickpea components
117 (starch). For this purpose, HHP-treated slurries were studied as a function of pressure level (0.1, 150, 300, 450,
118 and 600 MPa at 25 °C for 15 min) and slurry concentration (1:5, 1:4, 1:3, and 1:2 flour-to-water ratios). HHP-
119 treated CF slurries were then pasted under both isothermal (at 75 and 90 °C) and non-isothermal (from 30 up to
120 90 °C) heating processes, and then analyzed for changes in their thermorheological properties.
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122 **2. Materials and methods**
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124 *2.1. Materials*

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126 Spanish chickpea (*Cicer arietinum* cv. Castellano) flour was a commercially available product donated by
127 the Los Pisones flour milling company (Zamora, Spain). CF was supplied packed in polyethylene pouches (500
128 g) and was stored in watertight containers (10 °C and 73 ± 3% relative humidity) until use. Mean values for
129 proximate analysis (g 100 g^{-1}) of CF samples (as analyzed by the AOAC method, 1984) were: moisture, 8.49 ±
130 0.34, total ash, 2.77 ± 0.24, and crude protein (N × 6.25), 20.64 ± 0.05.

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132 *2.2. Sample preparation*

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134 CF slurries were prepared at different flour concentrations yielding 1:5, 1:4, 1:3, and 1:2 flour-to-water
135 ratios. The required amounts of chickpea flour and distilled water were placed in a 250-ml beaker, hand mixed
136 with a glass rod, and kept for half an hour at room temperature (25 ± 1 °C) for hydration with stirring at 900 rpm
137 before subjecting each sample to the HHP treatments.

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139 *2.3. High hydrostatic pressure treatment*

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141 CF slurries (200 ml) were vacuum packaged in a very low gas permeability bag type, Doypack® (Polyskin
142 XL, Flexibles Hispania, S.L.). Packed samples were vacuum-packed one more time to prevent contact between
143 pressurization fluid and slurry. HHP treatment was performed using a Stansted Fluid Power Iso-lab 900 High
144 Pressure Food Processor (Model: FPG7100:9/2C, Stansted Fluid Power Ltd., Harlow, Essex, UK), with 2925 ml
145 capacity, maximum pressure of 900 MPa, and a potential maximum temperature of 100 °C. Four packed samples
146 were introduced simultaneously into the pressure unit filled with pressure medium (water), then treated at
147 pressures of 150, 300, 450, or 600 MPa, and compared with untreated samples. Pressure was increased at a rate
148 of 500 MPa/min and maintained at the desired pressure for a holding time of 15 min; the decompression time
149 was less than 4 s. The temperature of the pressure unit vessel was thermostatically controlled at 25 °C
150 throughout all the treatments. Pressure, time, and temperature were controlled by a computer program, being
151 constantly monitored and recorded during the process. Representations of the variation of temperature and
152 pressure vs. time during the various HHP treatments are shown in Fig. 1. Increases of up to a maximum of 4 °C,
153 8 °C, 11 °C, or 15 °C ± 1 °C at 150, 300, 450, or 600 MPa, respectively, due to compressive heating, were

observed in the temperature of the pressuring fluid, but they were transient and equilibrated at 25 ± 2.5 °C during the holding period at those pressure levels. The average adiabatic heating during pressurization was ~2.5 °C/100 MPa. The temperature was more accurately equilibrated at 25 °C at the highest pressure applied (Fig. 1). After HHP treatment, samples were immediately stored at 4 °C for further use. All the HHP treatments were performed twice (two batches).

2.4. Rheological measurements

A Bohlin CVR 50 controlled stress rheometer (Bohlin Instruments Ltd., Cirencester, UK) was used to conduct small amplitude oscillatory shear (SAOS) measurements under isothermal and non-isothermal heating conditions in combination with a four-bladed cruciform vane geometry (diameter = 25 mm and height = 40 mm), rotating inside a 27-mm-diameter serrated cup with serrations 0.5 mm deep, and a solvent trap to minimize moisture loss during tests. SAOS isothermal measurements were carried out at three selected temperatures (25, 75, and 90 °C). The temperature of the sample was controlled internally via a computer using a Bohlin Rheology fluid circulating bath KTB-30 (also from Bohlin Instruments Ltd.). Dynamic rheological measurements under isothermal conditions were carried out at three selected temperatures (25, 75, and 90 °C). At 25 °C, CF slurry was allowed to rest for 5 min for stress relaxation and temperature equilibration before the actual measurements.

2.4.1. SAOS measurements under isothermal heating

CF slurry was pasted under isothermal heating conditions in the vane geometry in situ maintained at 75 and 90 °C, using the pre-condition option for 15 and 5 min, respectively, with controlled amplitude of the periodic shear stress (σ) at 0 Pa (without imposed stress) before the actual measurements. SAOS measurements on thermally induced CF paste were carried out at the same temperatures as those selected for paste induction (i.e., 75 and 90 °C). Paste induction temperatures were selected on the basis of gelatinization temperature ranges of CF slurries as observed by differential scanning calorimetry (DSC) thermograms. To select appropriate paste induction times for each temperature, CF slurries were isothermally heated to 75 and 90 °C and held for 30 min (time sweep tests). Under isothermal heating, times of 15 and 5 min at 75 and 90 °C, respectively, were considered appropriate to ensure suitable paste formation from CF slurries at the flour-to-water ratios studied (data not shown).

In order to ensure that all measurements were carried out within the linear viscoelastic (LVE) range, initially oscillation stress amplitude sweeps were tested at 1 rad s^{-1} for selected flour-to-water ratios and temperatures. Amplitude sweeps were conducted by varying the σ of the input signal from low (1.23 Pa) to high levels, depending on flour concentration, namely: 300 Pa for 1:5 flour-to-water ratio; 350 Pa for 1:4 ratio; 500 Pa for 1:3 ratio, and 1200 Pa for 1:2 ratio. On the basis of these tests, oscillation stresses for the various flour contents and isothermal heating treatments were selected. Then frequency sweep tests were performed at variable frequencies over the range 0.1–100 rad s^{-1}, keeping the σ signal at a constant value within the LVE region. The elastic modulus (G', Pa), viscous modulus (G'', Pa), phase angle (δ, °), and complex viscosity (η^*, Pa s) values at a frequency of 1 rad s^{-1} were chosen for comparison of results. For CF slurry at 25 °C, frequency sweeps were carried out over the same frequency range, but maintaining the σ signal at the minimum value provided by the rheometer for vane geometry (1.23 Pa).

Given that the appearance of the data on logarithmic coordinates was nearly linear at 75 and 90 °C, a power law model was used to characterize the frequency (ω) dependence of the elastic and viscous moduli as follows (Eqs. (1) and (2)):

$$G' = G'_0 \, \omega^{n'} \quad (1)$$

$$G'' = G''_0 \, \omega^{n''} \quad (2)$$

where G'_0 (Pa) and G''_0 (Pa) are elastic and viscous moduli at 1 rad s^{-1}, respectively, and exponents n' and n'' (both dimensionless) denote the influence of ω on both moduli (Campo-Deaño, Tovas, Pombo, Solas, & Borderías, 2009). The difference ($G'_0 - G''_0$) was also used as a measure of *gel strength* (Campo-Deaño & Tovar, 2008).

2.4.2. SAOS measurements under non-isothermal heating

Following an initial equilibration of CF slurry for 5 min at 30 °C, temperature sweep tests were performed at a heating rate of 2 °C min^{-1} to an endpoint of 90 °C at an ω of 1 rad s^{-1}, with the σ signal at a constant value of 25 Pa. The η^* was monitored, resulting in a pasting profile. Several parameters, providing information on gelatinization characteristics, were extracted from the pasting curves. η^*_o and T_o are the complex viscosity and temperature, respectively, at the beginning of the viscosity increase and thus at the starting point of gelatinization. The end point is reached when η^* reaches a maximum, η^*_c, at temperature T_c, as described by

Vallons & Arendt (2009a). The breakdown was calculated as the decrease (%) in complex viscosity between η^*_c and the η^* at the final temperature of 90 °C.

All rheological measurements were carried out in triplicate for each batch (six replicates were measured). The G', G'', δ, and η^* values were obtained directly from the computer software supplied by the manufacturer (Rheometer Software v. 06.40, Bohlin Instruments Ltd.).

2.5. Thermal properties

A differential scanning calorimeter (TA Q1000, TA Instruments, New Castle, DE, USA) was employed to provide the thermal analysis of the chickpea slurries. It was calibrated with indium and sapphire for temperature and heat capacity values. Slurry samples, weighing around 15 mg (± 0.002) as measured by an electronic balance (Sartorious ME235S, Goettingen, Germany), were capsulated in aluminum hermetically sealed volatile pans. Thermal scans were performed from 25 to 150 °C at a heating rate of 10 °C min^{-1}. An empty pan was used as a reference, and dry nitrogen at a flow rate of 50 ml min^{-1} was used as the purge gas. Thermal transitions of CF slurries were measured in terms of onset (T_o), peak (T_p), and conclusion (T_c) gelatinization temperatures. The gelatinization temperature range (R) was computed as ($T_c - T_o$). The enthalpy (ΔH_{gel}) of the transition (associated with starch gelatinization) was calculated from the area of the peak endotherm using the Universal Analysis 2000 software (v. 4.1D, TA Instruments, New Castle, DE, USA). The peak height index (PHI) was calculated by the ratio $\Delta H_{gel}/(T_p - T_o)$, as described by Kaur and Singh (2005). In accordance with Vallons and Arendt (2009a, b), the degree of gelatinization was calculated using the following equation:

Degree of gelatinization (%) = $\{(\Delta H_{us} - \Delta H_{ts})\Delta H_{us}^{-1}\} \times 100$

where ΔH_{us} and ΔH_{ts} are the melting enthalpies of unpressurized and treated slurries, respectively. The DSC measurements were performed in triplicate for each batch (six replicates were measured).

2.6. Statistical analysis

To establish the effects of HHP treatment on the thermorheological properties of CF slurry and thermally induced paste at each flour-to-water ratio separately, as well as the effect of the slurry concentration at each pressure level studied, two one-factor ANOVAs were performed separately. The mean values shown were

obtained from two batches of HHP-treated samples and three replicates measured for each batch. Minimum significant differences were calculated by Fisher's least significant difference tests at a significance level of 0.01. Statistical analyses were carried out using the SPSS 19.0 statistical software package (SPSS, Inc., Chicago, IL, USA).

3. Results and discussion

3.1. Effect of HHP treatment and concentration on mechanical spectra of CF slurry and heat-induced paste under isothermal heating

Mechanical spectra obtained at 25 °C for untreated and HHP-treated (150, 300, 450, and 600 MPa at 25 °C for 15 min) CF samples at the highest concentration (1:2) are shown in Fig. 2. More concentrated slurries were found to be more affected by HHP treatment than the other concentrations. The behavior of unpressurized and pressurized dispersions at 25 °C resembled that of an entangled system, with $G'' > G'$ until the cross-over frequency (ω) was reached. It has been reported that an entanglement network system shows G'' and G' curves intersecting at the middle of the ω range, indicating a clear tendency for more solid-like behavior at higher frequencies (Ross-Murphy, 1984). Additionally, cross-over ω typically moved to higher ω values when the HHP level increased (Fig. 2). Rheological properties of CF slurries are presented in Table 1 as a function of HHP treatment at each flour-to-water ratio. For the same HHP treatment, the effect of flour-to-water ratio on the δ, G', and G'' values can also be observed. In general terms, the slurries exhibited gradual increases in both G' and G'' moduli with pressure applied and flour concentration, indicative of the presence of higher entanglement density, reflecting the fact that treatment of chickpea slurries with increasing HHP causes an increase in starch gelatinization, in agreement with previous findings in other either starch- or flour-in-water suspensions (Ahmed et al., 2007, 2009; Bauer & Knorr, 2005; Oh et al., 2008a, b; Vallons & Arendt, 2009a, b).

In any case, there were differences in the effects of HHP on rheological properties depending on slurry concentration. For samples containing flour-to-water ratios of 1:5, 1:4, and 1:3, the HHP treatment had a more significant effect on G'' (liquid-like property indicator or viscosity) values than on G' (indicator of mechanical strength of gel or elasticity) values. In contrast, for samples at lower concentrations (1:5 and 1:4), G' was almost independent of pressure (Table 1). More interestingly, at any given flour-to-water ratio, samples treated at 600 MPa showed a significant increase in their G'' values as compared with unpressurized slurries. For samples at 1:3

and 1:2 ratios, the increase in elasticity at 600 MPa was also found to be significant, indicating an increase in molecular interactions and a strengthening of flour structure with increasing pressure. The relationship between initial apparent viscosity and HHP followed a sigmoidal-shaped curve in both normal and waxy rice starch, which seems be typical of pressure-induced starch gelatinization (Oh et al., 2008b). The initial viscosity value did not change markedly until a critical level of pressure was applied, which was approximately 350 MPa for normal rice and 300 MPa for waxy rice starch. According to those authors, the sigmoidal-shaped gelatinization curve means that pressure-induced gelatinization occurred over a pressure range and that the treatment pressure had to be above a critical level for gelatinization to occur effectively. Bauer and Knorr (2005) also reported similar sigmoidal curves for pressure-induced gelatinization of wheat and tapioca starches. In this study, both G' and G'' values at 25 °C increased sharply between 450 and 600 MPa, indicating that a critical level of pressure could be at ~450 MPa for the CF slurries treated at 25 °C for 15 min. In addition, at the highest concentration (1:2), G' was influenced more than G'', resulting in a significant decrease in phase angle (δ) values as pressure level increased, supporting a higher elastic nature of samples with less moisture content and treated at 600 MPa. Stolt et al. (2001) found a complete loss of birefringence in barley starch after HHP treatment at 600 MPa for 15 min. HHP-induced melting of sorghum starch granules started at pressures > 300 MPa and complete gelatinization was obtained after treatment with 600 MPa (Vallons & Arendt, 2009a). HHP treatment also significantly increased both the elastic and viscous moduli of wheat flour slurries at 40% w/w (Vallons & Arendt, 2010). Similarly, basmati rice flour dispersions exhibited a gradual liquid-solid gel transformation as they gelatinized and/or denatured and behaved as a viscoelastic fluid without and following HHP treatment (Ahmed et al., 2007).

A dispersion can be converted into a paste/gel under suitable processing conditions, such as temperature change, and G' and complex viscosity (η^*) are good indices to characterize the gel that is formed (Kapri & Bhattacharya, 2008). Consequently, CF slurries were pre-treated with HHP and subsequently analyzed for changes in mechanical properties under isothermal heating carried out at either 75 or 90 °C. As an example, stress sweeps of heat-induced CF pastes containing a flour-to-water ratio of 1:4 after pressurization at 150 MPa are shown in Fig. 3. This is an appropriate test for analyzing the gel character ($G' > G''$) of samples, because as long as the strain amplitudes are below the limiting value (γ_{max}) the complex modulus (G^*, measurement of the overall resistance (elastic and viscous)) pattern has a plateau value, indicating that the gel structure is stable under these conditions (Alvarez, Fernández, Olivares, & Canet, 2012). According to the authors just cited, γ_{max} is defined as the strain above which G^* decreases by more than 10% of the G^*_{max} value. After isothermal heating

processes, the transition from a sol to a paste was evident from the changes in G' and G'' values. After all the HHP treatments applied, pastes heat-induced at 75 °C had higher G' values than those induced at 90 °C (Fig. 3); this reflects an increased resistance to shear forces in the pastes obtained by heating at 75 °C for 15 min, which were more rigid than those induced at 90 °C for 5 min. Similarly, an increase in flour concentration and isothermal heating time increased rice flour gel strength (Kapri and Bhattacharya, 2008).

Mechanical spectra of CF pastes heat-induced at 75 °C in the complete flour concentration range studied for untreated and HPP-treated samples are presented in Fig. 4. Similar results were obtained for pastes heat-induced at 90 °C. Slopes and intercepts of Eqs. (1) and (2) after linearization are shown in Tables 2 and 3 as a function of HHP treatment at each slurry concentration for CF pastes heat-induced at 75 and 90 °C, respectively. The CF pastes mostly exhibited solid-like characteristics, with higher magnitudes of G'_0 than G''_0. The ranges of the corresponding n' and n'' values were 0.04–0.07 and –0.01–0.14 for pastes induced at 75 °C, and 0.06–0.10 and 0.04–0.12 for those induced at the higher temperature. The negative n'' value obtained for the CF pastes heat-induced at 75 °C after HHP treatment with 450 MPa (Table 2) is due to the fact that the G'' curves tended to be concave at lower frequencies (Fig. 4c). Therefore, G' was relatively independent of frequency, while G'' was slightly dependent on frequency, which is associated with weak gel behavior. From a structural point of view, it is reported that for true gels $\ln\omega$ versus $\ln G'_0$ and $\ln G''_0$ have zero slopes (Ross-Murphy, 1984), whereas for weak gels, the plots result in positive slopes. Moreover, CF pastes heat-induced at 75 °C containing flour-to-water ratios of 1:3 and 1:2 exhibited stronger three-dimensional networks than those induced at 90 °C because the associated G'_0, G''_0, and $(G'_0 - G''_0)$ values were higher (Tables 2 and 3). Water probably becomes a critical factor below a flour-to-water ratio of 1:4, and therefore the gelatinization process of CF samples containing higher concentrations (1:3 and 1:2) remained incomplete after 5 min at 90 °C. In the case of 18% rice flour dispersions, gel formation took longer than for a 10% sample because of high solid content (Kapri & Bhattacharya, 2008).

Nevertheless, from Fig. 4 it is evident that HHP combined with thermal treatment resulted in a significant reduction in chickpea paste rigidity as compared with unpressurized samples. In most cases, the elasticity of thermally induced CF paste increased significantly as a function of slurry concentration and decreased with increasing pressure applied in proportion with the extent of HHP-induced gelatinization of starch (Tables 2 and 3). Gelatinization has been defined as an irreversible melting phase transition of starch granules from an ordered to a disordered state, which takes place in an excess of water (Bauer & Knorr, 2005; Hermansson & Svegmark, 1996; Oh et al., 2008b; Vallons & Arendt, 2009a). Consequently, weaker pastes are formed in the subsequent

heating process, because there is an increase in the amount of starch pre-gelatinized by pressure and the pastes are formed solely by melting of the crystallites that still remain. In addition, the effect of HHP treatment was more pronounced and significant at the lowest concentration (1:5). CF slurries containing a flour-to-water ratio of 1:5, pre-treated with the higher pressures and subsequently heated at 75 °C, did not show weak gel behavior (Fig. 4a), indicating that preliminary HHP treatment at either 450 or 600 MPa induced an elevated degree of starch gelatinization. For this reason, these slurries behaved as macromolecular solutions with no ability to form a gel under later isothermal heating, as reflected by the negative values of $\ln G'_0$ and $\ln G''_0$ obtained for these samples (Table 2), which correspond to a liquid-like behavior. Similar behavior was observed for the CF slurries at the lowest concentration pressurized at 600 MPa and subsequently heated at 90 °C (Table 3). On the other hand, this result would also indicate that CF slurry at the lowest concentration has a higher degree of gelatinization during pressurization (until the minimum required water level is reached) compared with the slurries with a lower moisture content. A similar observation was made by Ahmed et al. (2007) in rice flour slurry following HHP treatment, and by Katopo et al. (2002) during a morphological study of selected HHP-treated starch samples. Moreover, samples containing a flour-to-water of 1:5 that were pre-treated at 150 MPa and then heated under both conditions had significantly higher G' and G'' values than unpressurized samples, suggesting that pressure-induced melting of granules started at pressures > 150 MPa. According to Oey et al. (2008), the increase in elasticity of the samples treated at the lowest pressure could be attributed to an increase in the linearity of the cell walls and volumes of particles owing to the permeability of the cell walls.

3.2. Effect of HHP treatment and concentration on pasting properties of CF slurry under non-isothermal heating

Changes in complex viscosity (η^*), defined by $G^*/i\omega$, were recorded during pasting while stirring the sample, to construct a pasting curve. Therefore, gelatinization was measured as an increase in resistance to flow. Similar pasting profiles were obtained from temperature sweeps for sorghum starch suspensions (Vallons & Arendt, 2009a), whereas for buckwheat starch suspensions G^* was monitored (Vallons & Arendt, 2009b). In turn, for various starch-in-water suspensions a starch cell was used and the pasting procedure entailed measuring the apparent viscosity of the samples (Oh et al., 2008a, b).

Pasting curves for unpressurized and pressurized CF slurries at the four concentrations studied are shown in Fig. 5, where η^* is given as a function of temperature. Significant differences were observed in pasting characteristics of CF slurries as a function of either flour-to-water ratio or pressure level, showing different

pasting patterns. The initial increase in temperature produced a decrease in η^* values that may be associated with the effect of increasing temperature during pasting. This decrease was more evident for samples at the highest concentration (Fig. 5d), in which the η^* values decreased considerably until the inflexion point in the curve was reached. CF slurries containing flour-to-water ratios of 1:3 and 1:2 displayed considerable increases in initial η^* after HHP treatment at 600 MPa compared with the untreated slurries, supporting the hypothesis that the degree of swelling increased with increasing pressure applied (Figs. 5c, d). The increase in initial viscosity after HHP treatment would indicate the degree of gelatinization of starch as a consequence of the HHP treatment (Oh et al., 2008b). The authors just cited observed that after 500 MPa at 40 °C for 30 min a waxy rice starch suspension showed an initial viscosity value that was slightly higher than the peak viscosity value of the untreated suspension, and the viscosity did not increase further during pasting, showing 100% swelling even at the lowest pressurization temperature (10 °C). However, the degree of gelatinization of both normal and waxy rice starches was dependent on the pressure, treatment temperature, and treatment time, and different combinations of these factors could result in the same degree of gelatinization, confirming previous findings (Bauer & Knorr, 2005).

For CF slurries, it can be observed that when either unpressurized or pressurized dispersions were heated up to 90 °C an increase in η^* occurred in all cases. Starch gelatinization involves granule swelling and release of starch material and results in an increase in viscosity (BeMiller & Whistler, 1996). In turn, partial gelatinization is observed when the initial viscosity of the HHP-treated starch suspension is higher than that of the untreated suspension, but the suspension still shows an increase in viscosity when temperature increases above onset gelatinization temperature (Oh et al., 2008a). Consequently, the pasting curves would seem to indicate that the CF slurries had not been completely gelatinized by the HHP treatments applied at 25 °C for 15 min.

However, it can be seen that for all the slurries pre-treated at 600 MPa the η^* increase was more gradual and over a wider temperature range. On the other hand, on pasting, the viscosities of the samples at the lowest concentration (1:5) pre-treated at 450 and 600 MPa increased to η^* values that were noticeably lower than the values achieved by the unpressurized samples (Fig. 5a). In view of the fact that frequency sweeps showed that CF slurries at the lowest concentration pressurized at 450 and 600 MPa were not able to form a paste/gel on isothermal heating (Table 2), this result might reflect a nearly complete gelatinization induced by HHP in these samples. The reduced increase in η^* could also basically be contributed by leaching of amylose during thermal heating, which was restricted in pressure gelatinization (Ahmed et al., 2007). Furthermore, breakdown of granules also accounted for the apparent increase in viscosity of HHP-treated samples during pasting (Oh et al., 2008b). In contrast, samples of sorghum starch pre-treated at 500 and 600 MPa showed no increase in viscosity,

and therefore a complete gelatinization induced by HHP treatment was assumed for these pre-treated starches by Vallons and Arendt (2009a). In any case, a different degree of gelatinization can be distinguished from the CF pasting profiles.

The gelatinization temperatures (T_o and T_c) and complex viscosities (η^*_o and η^*_c) extracted from pasting curves are shown in Table 4. Both flour reduction and pressurization significantly affected the temperature at which the inflexion point in the curve appeared, as the presence of higher water content increased the starch gelatinization temperature, while the presence of pre-gelatinized granules in slurries treated at 600 MPa decreased it. Moreover, in the 1:5 ratio control slurry the inflexion point occurred at approximately 73 °C, while the HHP treatment at 600 MPa decreased it to approximately 60 °C. In turn, the T_o for unpressurized 1:2 ratio slurry was 65 °C and decreased to 38 °C after HHP treatment with 600 MPa. Similarly, for pressure treatment, T_o decreased with increasing degree of pre-gelatinized sorghum starch (Vallons & Arendt, 2009a). The end point of gelatinization is reached when η^* reaches a maximum, η^*_c, at temperature T_c. For samples containing flour-to-water ratios of 1:5 and 1:4, a well-defined maximum complex viscosity (peak value) could not be detected because η^* continued to increase gradually up to the final temperature of 90 °C (Fig. 5). Therefore, T_c was considered to be 90 °C for the more dilute slurries, and the η^*_c values coincided with the η^* at the final temperature of 90 °C (Table 4). In contrast, more concentrated CF slurries showed a peak viscosity indicating destruction of gel structure during prolonged heating, as reported earlier (Lii, Shao, & Tseng, 1995). In addition, for the more concentrated slurries the increase in η^* was more rapid, so that T_c was lower than 90 °C, and practically unaffected by pressure treatment. Both T_o and T_c of the 1:2 ratio slurry decreased compared with the 1:3 ratio slurry, indicating that the gelatinization process occurred at a lower temperature range because of high solid content.

CF slurries treated at 600 MPa showed a significant increase in η^*_o values compared with unpressurized samples regardless of slurry concentration, which is again associated with increasing amounts of pre-gelatinized granules (Vallons & Arendt, 2009a). The η^*_o for untreated CF slurries at 1:5 and 1:4 ratios was 0.017 Pa s and was not significantly different from the η^*_o values after HHP treatment at ≤ 450 MPa. For these more dilute slurries, the η^*_o value increased to 0.021 and 0.031 Pa s, respectively, after HHP treatment at 600 MPa. The initial η^* value of normal rice starch was 0.007 Pa s when untreated, and increased to 0.043 Pa s after treatment at 500 MPa (Oh et al., 2008b). Similarly, for 1:3 ratio chickpea slurry the η^*_o value did not change significantly until the level of 600 MPa, reaching a value of 2 Pa s. In turn, η^*_o increased significantly from 0.035 (untreated) to 43 Pa s (600 MPa) for samples at the highest concentration (1:2). As a result of adiabatic heating (~2.5 °C/100

MPa), the temperature increased by up to 15 °C at 600 MPa and then decreased back to the set temperature within 8 min of the set holding time of 15 min (Fig. 1). At 600 MPa, as T_o was 38 °C for samples at the highest concentration (Table 4), the temperature of the unit stayed near T_o, explaining the significant increase observed in η^*_o. In addition, for the same flour-to-water ratio a significant lower η^*_c was observed after HHP treatment at 600 MPa, indicating that η^* did not increase to the η^*_c that was attained on pasting compared with the untreated samples. Katopo et al. (2008) also reported that the peak viscosity of pressure-treated waxy corn starch was lower than that of the untreated sample and related this to changes of granular structures during the transformation of crystalline structure and to the development of an amylose-lipid complex under HHP, which then associated with amylopectin molecules to restrict swelling and dispersion of the starch granules. Finally, when heated above T_c, CF pastes induced from more concentrated slurries showed a decrease in η^*, and the breakdown decreased significantly as the pressure applied increased. In contrast, a breakdown value could not be estimated for CF pastes induced from more dilute slurries. The non-existence of structural breakdown during heating would reflect very high stability of the pastes induced from less concentrated CF slurries (Arocas, Sanz, & Fiszman, 2009; Kaur & Singh, 2005). Furthermore, CF at 1:5 and 1:4 ratios swells slowly on heating, tending to be not very shear sensitive (Arocas et al., 2009). These results show that a suitable selection of HHP treatment at appropriate levels can produce chickpea pastes with more advantageous handling properties, leading to the development of new products, although further studies are required to determine the significance of pressure, temperature, and time combinations on the degree of gelatinization of CF slurry.

3.3. Effect of HHP treatment and concentration on thermal properties of CF slurry

CF samples were thermally scanned in a differential scanning calorimeter up to 150 °C, and typically exhibited a single endothermic peak associated with gelatinization of C-type crystals (Aguilera et al., 2009). This observation was supported by earlier studies reporting a single DSC endotherm for starch gelatinization in the presence of excess water (Calzetta Resio & Suarez, 2001). Nevertheless, pressure-induced gelatinization of granules started at a pressure of 150 MPa, although the endothermic peak disappeared after HHP treatment at 600 MPa, suggesting complete starch gelatinization induced by a sufficiently high pressure (Vallons & Arendt, 2009a, b). Similar results were previously observed by other authors. Stolt et al. (2001) found a complete loss of birefringence in 5% barley starch suspension after a 15-min pressure treatment at 600 MPa and 20 °C. For rice

and sorghum starches, an endothermic gelatinization peak was not observed after HHP treatments at 650 and 600 MPa, respectively (Ahmed et al., 2007; Vallons & Arendt, 2009a).

The effect of pressure level and flour-to-water ratio on the thermal properties of CF slurry is illustrated in Table 5. Significant differences ($P < 0.01$) were observed in all thermal properties among the various flour contents. At constant pressure, T_o increased with increasing slurry concentration. At low moisture content the plasticizing effect of water is low, which leads to a high crystallite gelatinization temperature (Ahmed et al., 2007). For samples containing a flour-to-water ratio of 1:5, T_o decreased significantly with increasing pre-treatment severity, whereas there was less difference between the T_o values of pre-treated CF slurries at higher concentrations. For samples of wheat and potato starches, reduction in temperature at which gelatinization took place was a non-linear function of pressure, being greatest at the highest water contents (Murh & Blanshard, 1982). On the other hand, the effect of HHP treatment on T_p and T_c was quite uncertain and depended on slurry concentration. For example, untreated 1:5 ratio CF slurry had significantly lower values of T_c than pressurized samples, the opposite of the effect observed for samples with a lower water content. Sorghum starch samples pretreated with 500 MPa for 10 min showed an increase of about 5 °C in all gelatinization temperatures (Vallons & Arendt, 2009a), whereas the T_p of rice flour slurry decreased systematically from 350 to 500 MPa after HHP treatment as compared with unpressurized sample (Ahmed et al., 2007). In addition, the T_c values of untreated CF slurry significantly increased with decreasing water content. The influence of water:starch ratio on gelatinization of amaranth starch was investigated using DSC (Calzetta Resio & Suarez, 2001). T_o and T_p did not vary significantly with increase in water content, whereas T_c decreased by more than 14 °C when water content increased. This was attributed to extensive hydration and swelling of the amorphous regions, which in turn enhances melting of crystallites upon heating.

Meares, Bogracheva, Hill, & Hedley (2004) reported average T_o and T_p of 64 and 72 °C, respectively, for Australian CF samples, similar to the present results obtained for unpressurized slurries. In turn, Kaur and Singh (2005) reported higher onset (65.4–67.9 °C) and similar peak (70.6–73.3 °C) temperatures for Indian Kabuli and Desi flours compared with those of the untreated Spanish chickpea variety in this study. This variation in thermal properties may be attributed to variations in the moisture content of the slurries. On the other hand, the onset gelatinization temperatures measured by DSC were lower than those obtained using temperature sweeps (Table 4), which can be explained by the properties measured by the two methods. While DSC measures gelatinization as melting of starch crystals, the rheometer measures gelatinization as an increase in viscosity (Vallons & Arendt, 2009a).

However, at constant pressure, the enthalpy value increased significantly as flour concentration increased (from 1:5 to 1:2) and decreased significantly with increasing pressure applied, indicating progressive gelatinization as pressure levels increased (Table 5). A decrease in ΔH_{gel} with pressure level has been reported in the literature for various starches (Ahmed et al., 2007, 2009; Katopo et al., 2002; Vallons & Arendt, 2009a, b). ΔH_{gel} of untreated CF slurries ranged from 2.1 to 4.5 J g^{-1}, highest for 1:2 and lowest for 1:5 flour-to-water ratio. Similar enthalpies (3.5–4.9 J g^{-1}) for Indian CF slurries were reported by Kaur and Singh (2005).

Different starch suspensions were qualitatively divided into three classes by Oh et al. (2008a): waxy starches, which can fully gelatinize at elevated HHP (> 400 MPa); normal starches, which partially gelatinize under HHP (up to the pressure of 600 MPa applied here), and HHP-resistant starches such as potato starch that are not affected by HHP treatment up to 600 MPa. On the basis of the rheological measurements, complete pressure-induced gelatinization could not be inferred for the more concentrated CF slurries. Therefore, using DSC to characterize gelatinization temperatures, the effect of HHP treatment on CF slurry could be associated with that of normal starches, probably as a result of increasing partial swelling of starch granules with increasing pressure level. It is also possible that at 1:3 and 1:2 ratios excessive pressure weakened the structure of ungelatinized granules, hindering swelling during subsequent heating. It has also been suggested that amylose–lipid complexes could be formed in normal starches and that these complexes may restrict the swelling of starch granules during heating in the differential scanning calorimeter (Katopo et al., 2002). In addition to starch, CF slurries contain a relatively large amount of protein, which could give a second endothermic peak on heating in water. HHP treatment of rice slurry resulted in a decreased gelatinization temperature as compared with untreated sample, and the presence of protein in rice flour slurry was considered responsible for this (Ahmed et al. 2007). In turn, overlapping protein and starch peaks in the CF thermogram made it impossible to determine the ΔH_{gel} and the width of the starch gelatinization transition (Meares et al., 2004). According to those authors, a heating rate of 10 °C min^{-1} could be too rapid to detect the endothermic transition of pre-gelatinized samples. At the temperature range used in this study, a second endothermic peak was detected for some CF slurries, although the study of the HHP effect was focused on the first endothermic peak.

However, DSC has been used to study starch retrogradation phenomena during HHP processing (Ahmed et al., 2007, 2009; Douzals, Perrier Cornet, Gervais, & Coquille, 1998; Stolt et al., 2001). The retrogradation of pressure-induced gels is supposed to differ from that of heat-induced gels because almost no leaching of amylose is observed after pressurization, and therefore the retrogradation occurs within the starch granules (Douzals, Perrier Cornet, Gervais, & Coquille, 1998). Pressure-treated lentil samples exhibited a relatively lower extent of

recrystallization than thermally treated slurry during storage (Ahmed et al., 2009). For retrogradation studies, 25% starch suspension was pressurized at 550 MPa and 30 °C for 10 min. This treatment induced a gel for which no endothermic peak was observed in the DSC thermogram immediately after pressurization (Stolt et al., 2001). However, after 1 day of storage at 4 °C a small broad peak – typical for retrogradation – appeared, and the enthalpy of the amylopectin crystals formed during storage increased with increasing storage time. In turn, Ahmed et al. (2007) reported that there was no retrogradation in HHP-treated starch samples during low temperature storage for 24 h. In the present work, half of the samples were scanned immediately after HHP treatment, whereas the other half were stored for 24 h at 4 °C prior to scanning. It is possible, therefore, that there was retrogradation in HHP-treated slurry samples during storage. More research is required to elucidate the origin of the second endotherm peak that appeared occasionally.

PHI is a measure of uniformity in gelatinization (Kaur & Singh, 2005). PHI values for the CF slurries increased significantly as concentration increased, but decreased significantly with increasing pressure applied (Table 5). At constant pressure, samples containing a flour-to-water ratio of 1:2 showed the significantly highest PHI values as compared with more dilute slurries. For samples at 1:4 and 1:2 ratios, significantly greater energy is also needed (fusion enthalpy) to break the intermolecular bonds in starch granules of CF slurries treated at 150 MPa to achieve gelatinization. This would explain why the G' and G'' values found in their mechanical spectra were higher than in the unpressurized and other pressurized samples (Table 2). In turn, unpressurized samples at the lowest concentration (1:5) had a lower gelatinization temperature range ($T_c - T_o$) than the samples treated at 450 MPa, whereas the opposite was observed for the other slurries. The large range for the most dilute slurry after treatment at 450 MPa suggests the presence of crystallites of varying stability within the crystalline domains of their starch granules (Kaur & Singh, 2005).

Finally, Table 5 also shows the degree of gelatinization of CF slurries estimated from the gelatinization ΔH_{gel} values. At constant slurry concentration, the ΔH_{gel} values decreased with increasing pressure, and consequently the percentage of gelatinized starch granules increased, which would explain why the elasticity of the subsequent heat-induced CF paste decreased. In view of the results of the rheological measurements, complete gelatinization (100%) was only associated with samples at the lowest concentration (1:5) after HHP with 600 MPa. However, more dilute slurry showed a smaller increase in degree of gelatinization at 450 MPa. It has been shown that pressure-induced starch gelatinization is highly sensitive to changes in temperature, pressure, and treatment time (Bauer & Knorr, 2005; Oh et al., 2008b). The effects of increasing temperature are essentially energy and volume effects due to thermal expansivity, whereas the effects of pressure are mainly

volume effects caused by compressibility of the system (Oh et al., 2008b). The higher the temperature, the lower the pressure of complete gelatinization, whereas at constant temperature and pressure the degree of gelatinization increases with increasing treatment time (Bauer & Knorr, 2005). It is possible, therefore, that longer pressure–time treatments or higher pressure–temperature treatments would be necessary to reach 100% swelling at 600 MPa for CF slurries at 1:4, 1:3, and 1:2 ratios. In addition, the degree of gelatinization had an obvious tendency to decrease with increasing slurry concentration, which was also supported by the higher elasticity associated with the CF pastes induced from more concentrated slurries. A linear relationship between the degree of swelling and initial apparent viscosity of starch suspensions after pressure treatments was observed previously (Oh et al., 2008b).

4. Conclusions

The behavior of the unpressurized and pressurized CF slurry at 25 °C resembled that of an entangled system, with $G'' > G'$ until the cross-over frequency was reached; the slurries underwent significant increases in viscoelasticity with increases in flour concentration and pressure applied. In turn, viscoelasticity of thermally induced CF paste increased as a function of slurry concentration and decreased with increasing pressure applied in proportion with the extent of HHP-induced gelatinization of starch. The effect of HHP treatment was more pronounced at the higher water contents. The gelatinization enthalpies of the HHP-treated slurries reflected progressive gelatinization as the pressure level increased, i.e., the enthalpy decreased with increasing pressure applied. The enthalpy value also increased with increasing slurry concentration. CF slurries subjected to 600 MPa at 25 °C for 15 min showed no peak and hence no enthalpy value, suggesting complete HHP-induced gelatinization of starch. However, viscoelastic properties revealed that probably only CF slurries containing a flour-to-water ratio of 1:5 were totally gelatinized after HHP-treatment at 600 MPa. For more concentrated CF slurries, HHP-induced gelatinization was partial, and the degree of swelling increased with pressure and decreased with increasing slurry concentration. Consequently, the strength of the CF pastes obtained fell with increasing pressure level. It remains unknown whether further changes can occur in CF slurry when treatment time, temperature, and pressure increase beyond the levels used in this study. In terms of industrial application, it has been observed that raw gel/paste formed by heating of chickpea in water is very hard if the objective is a paste that is to be flattened/rolled/sheeted/shaped to make different products. It is possible that the addition of

HHP-treated CF slurries (600 MPa at 25 °C for 15 min) to unpressurized similar batter-based products would offer easier flow characteristics during heating, preparation, and handling.

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662

663 **Figure captions**

664

665 **Fig. 1.** Representation of the temperature and pressure vs. time variation during HHP treatments (150, 300, 450,
666 and 600 MPa at 25 °C for 15 min).

667 **Fig. 4.** Typical mechanical spectra of pressurized (200 MPa at 10 °C for 5, 15, and 25 min) chickpea flour slurry
668 after non-isothermal heating from 25 to 95 °C and cooling down to 25 °C. Mean values of six measurements ±
669 error bars.

670 **Fig. 3.** Typical stress sweep showing the changes in elastic modulus (*G*'), viscous modulus (*G*''), and complex
671 modulus (*G**) with strain (frequency 1 rad s^{-1}) for heat-induced pastes of pressure treated (150 MPa at 25 °C for
672 15 min) chickpea flour slurry containing a flour-to-water ratio of 1:4 at 75 and 90 °C.

673 **Fig. 4.** Effect of high hydrostatic pressure (HHP) treatment on mechanical spectra of chickpea flour paste heat-
674 induced at 75 °C containing flour-to-water ratios of (a) 1:5, (b) 1:4, (c) 1:3, and (d) 1:2. Mean values of six
675 measurements ± error bars.

676 **Fig. 5.** Effect of high hydrostatic pressure (HHP) treatment on pasting properties of chickpea flour slurry
677 containing flour-to-water ratios of (a) 1:5, (b) 1:4, (c) 1:3, and (d) 1:2.

Table 1

Effect of high hydrostatic pressure treatment (at 25 °C for 15 min) and slurry concentration on oscillatory rheological properties of chickpea flour slurry at 25 °C.

High pressure (MPa)	Ratio (flour-to-water)	δ (°)	G' (Pa)	G'' (Pa)
0.1	1:5	$58.0\pm5.1^{a,bC}$	0.0051 ± 0.0009^{aA}	$0.0082\pm0.0003^{b,cC}$
150		53.2 ± 6.1^{bB}	$0.0052\pm0.0008^{aA,B}$	0.0069 ± 0.0006^{cC}
300		$58.9\pm4.5^{a,bC}$	0.0051 ± 0.0009^{aA}	0.0084 ± 0.0005^{bC}
450		$63.0\pm1.3^{a,bC}$	0.0048 ± 0.0005^{aA}	0.0094 ± 0.0004^{bC}
600		67.9 ± 2.4^{aB}	0.0050 ± 0.0005^{aB}	0.0122 ± 0.0003^{aB}
0.1	1:4	$64.3\pm1.5^{b,cC}$	$0.0050\pm0.0004^{a\text{-}cA}$	$0.0104\pm0.0001^{b,cC}$
150		52.2 ± 8.4^{cB}	0.0060 ± 0.0004^{aA}	0.0080 ± 0.0019^{cC}
300		66.9 ± 1.9^{bC}	$0.0044\pm0.0002^{b,cA}$	$0.0104\pm0.0007^{b,cC}$
450		67.5 ± 2.4^{bC}	$0.0054\pm0.0008^{a,bA}$	0.0130 ± 0.0004^{bC}
600		87.0 ± 0.3^{aA}	0.0038 ± 0.0003^{cB}	0.0744 ± 0.0013^{aB}
0.1	1:3	74.5 ± 0.4^{dB}	0.0043 ± 0.0001^{bA}	0.0156 ± 0.0002^{cB}
150		74.6 ± 0.5^{dA}	0.0043 ± 0.0001^{bB}	0.0157 ± 0.0004^{cB}
300		77.1 ± 1.2^{cB}	0.0045 ± 0.0005^{bA}	$0.0199\pm0.0005^{b,cB}$
450		80.5 ± 0.9^{bB}	0.0044 ± 0.0004^{bA}	0.0263 ± 0.0003^{bB}
600		86.7 ± 0.0^{aA}	0.0094 ± 0.0002^{aB}	0.1630 ± 0.0044^{aB}
0.1	1:2	89.2 ± 0.2^{aA}	0.0010 ± 0.0002^{bB}	0.0707 ± 0.0018^{bA}
150		88.4 ± 0.0^{bA}	0.0018 ± 0.0000^{bC}	0.0641 ± 0.0003^{bA}
300		87.6 ± 0.1^{cA}	0.0035 ± 0.0001^{bA}	0.0824 ± 0.0018^{bA}
450		$87.8\pm0.2^{b,cA}$	0.0043 ± 0.0001^{bA}	0.1128 ± 0.0061^{bA}
600		49.9 ± 0.4^{dC}	8.6 ± 0.4^{aA}	10.2 ± 0.3^{aA}

Mean values (n = 6) ± SD.

[a-d]For each rheological property and for the same flour-to-water ratio, means without the same letter are significantly different ($P < 0.01$) according to the LSD multiple range test.

[A-C]For each rheological property and for the same high hydrostatic pressure treatment, means without the same letter are significantly different ($P < 0.01$) according to the LSD multiple range test.

δ, phase angle; G', storage modulus; G'', loss modulus; mean values are given at 1 rad s^{-1}.

Table 2
Effect of high hydrostatic pressure treatment (at 25 °C for 15 min) and slurry concentration on power law parameters of Eqs. (1) and (2) from frequency sweep tests of chickpea paste heat-induced at 75 °C.

High pressure (MPa)	Ratio (flour-to-water)	$\ln G' = \ln G'_0 + n' \ln\omega$ Eq. (1)		$\ln G'' = \ln G''_0 + n'' \ln\omega$ Eq. (2)		$G'_0 - G''_0$ (Pa s^n)
		$\ln G'_0$ (Pa $s^{n'}$)	n'	$\ln G''_0$ (Pa $s^{n''}$)	n''	
0.1	1:5	5.87 ± 0.02^{dD}	$0.05\pm0.001^{bA,B}$	4.30 ± 0.01^{dD}	0.11 ± 0.005^{cA}	279.5 ± 7.3^{bC}
150		6.82 ± 0.03^{cC}	0.04 ± 0.001^{bC}	4.48 ± 0.02^{cD}	0.14 ± 0.006^{bA}	825.0 ± 27.5^{aC}
300		5.12 ± 0.08^{bD}	0.05 ± 0.009^{bA}	3.31 ± 0.01^{bD}	$0.09\pm0.005^{cA,B}$	140.7 ± 13.1^{cC}
450		-4.64 ± 0.04^{aD}	1.60 ± 0.035^{aA}	-2.85 ± 0.26^{aD}	0.99 ± 0.009^{aA}	-
600		-4.54 ± 0.09^{aD}	1.64 ± 0.010^{aA}	-3.36 ± 0.01^{aD}	0.98 ± 0.018^{aA}	-
0.1	1:4	$6.81\pm0.04^{a,bC}$	0.05 ± 0.003^{bB}	4.58 ± 0.03^{bC}	0.11 ± 0.010^{aA}	$811.5\pm39.5^{a,bC}$
150		6.86 ± 0.04^{aC}	$0.04\pm0.002^{bB,C}$	$4.64\pm0.01^{a,bC}$	$0.12\pm0.007^{aA,B}$	848.5 ± 36.1^{aC}
300		6.72 ± 0.03^{bC}	0.04 ± 0.001^{bA}	4.59 ± 0.03^{bC}	0.11 ± 0.012^{aA}	728.8 ± 26.1^{bC}
450		4.93 ± 0.04^{dC}	0.04 ± 0.004^{bB}	3.83 ± 0.04^{cC}	0.06 ± 0.012^{bB}	92.0 ± 4.2^{dC}
600		6.07 ± 0.05^{cC}	0.06 ± 0.000^{aB}	4.73 ± 0.02^{aC}	0.03 ± 0.012^{bB}	321.3 ± 19.2^{cB}
0.1	1:3	7.98 ± 0.04^{aB}	$0.05\pm0.003^{bA,B}$	5.71 ± 0.02^{aB}	0.10 ± 0.008^{aA}	2617.2 ± 122.8^{aB}
150		7.83 ± 0.04^{aB}	$0.05\pm0.002^{bA,B}$	5.59 ± 0.01^{bB}	0.10 ± 0.010^{aB}	2249.6 ± 102.0^{bB}
300		7.92 ± 0.04^{aB}	0.05 ± 0.003^{bA}	5.75 ± 0.03^{aB}	0.08 ± 0.015^{aB}	$2438.8\pm116.8^{a,bB}$
450		7.37 ± 0.09^{bB}	0.07 ± 0.008^{aB}	$5.69\pm0.02^{a,bB}$	-0.01 ± 0.004^{bD}	1301.3 ± 132.0^{cB}
600		6.80 ± 0.03^{cB}	$0.06\pm0.005^{a,bB}$	5.49 ± 0.06^{cB}	0.08 ± 0.017^{aB}	651.7 ± 25.3^{dB}
0.1	1:2	9.32 ± 0.06^{aA}	0.06 ± 0.003^{aA}	7.08 ± 0.01^{aA}	$0.07\pm0.009^{b,cB}$	9934.4 ± 663.0^{aA}
150		9.32 ± 0.06^{aA}	0.05 ± 0.004^{aA}	6.97 ± 0.00^{bA}	0.10 ± 0.001^{aB}	10152.1 ± 619.5^{aA}
300		9.35 ± 0.03^{aA}	0.05 ± 0.002^{aA}	7.09 ± 0.01^{aA}	$0.09\pm0.005^{a,bA,B}$	10257.4 ± 402.1^{aA}
450		9.04 ± 0.06^{bA}	0.06 ± 0.007^{aB}	7.10 ± 0.02^{aA}	0.02 ± 0.007^{dC}	7260.5 ± 555.4^{bA}
600		9.05 ± 0.05^{bA}	0.05 ± 0.003^{aB}	6.92 ± 0.04^{bA}	0.06 ± 0.014^{cB}	7506.7 ± 441.0^{bA}

Mean values (n = 6) ± SD.
[a-d]For each rheological parameter and for the same flour-to-water ratio, means without the same letter are significantly different ($P < 0.01$) according to the LSD multiple range test.
[A-D]For each rheological parameter and for the same high hydrostatic pressure treatment, means without the same letter are significantly different ($P < 0.01$) according to the LSD multiple range test.
$\ln G'_0$, $\ln G''_0$, n', and n'', regression coefficients relating G' or G'' and frequency (ω). $G'_0 - G''_0$, gel strength.

Table 3

Effect of high hydrostatic pressure treatment (at 25 °C for 15 min) and slurry concentration on power law parameters of Eqs. (1) and (2) from frequency sweep tests of chickpea paste heat-induced at 90 °C.

High pressure (MPa)	Ratio (flour-to-water)	$\ln G' = \ln G'_0 + n' \ln\omega$ Eq. (1)		$\ln G'' = \ln G''_0 + n'' \ln\omega$ Eq. (2)		$G'_0 - G''_0$ (Pa s^n)
		$\ln G'_0$ (Pa $s^{n'}$)	n'	$\ln G''_0$ (Pa $s^{n''}$)	n''	
0.1	1:5	5.98 ± 0.00^{bD}	$0.07\pm0.004^{bA,B}$	4.38 ± 0.03^{bD}	$0.06\pm0.005^{bA,B}$	317.6 ± 2.5^{bD}
150		6.58 ± 0.02^{aD}	0.06 ± 0.004^{bB}	4.61 ± 0.04^{aD}	0.10 ± 0.005^{bA}	619.6 ± 14.5^{aC}
300		5.48 ± 0.06^{cD}	0.06 ± 0.012^{bA}	4.06 ± 0.02^{cD}	0.10 ± 0.009^{bA}	181.2 ± 13.1^{cC}
450		5.23 ± 0.02^{dD}	0.08 ± 0.007^{bA}	3.91 ± 0.01^{dD}	0.10 ± 0.006^{bA}	136.6 ± 3.6^{dD}
600		-5.06 ± 0.01^{eD}	1.75 ± 0.006^{aA}	-2.79 ± 0.02^{eD}	0.97 ± 0.032^{aA}	-
0.1	1:4	6.70 ± 0.04^{aC}	$0.07\pm0.007^{a,bA,B}$	4.89 ± 0.03^{aC}	0.06 ± 0.008^{cA}	676.7 ± 33.2^{aC}
150		6.67 ± 0.01^{aC}	$0.06\pm0.003^{bA,B}$	4.74 ± 0.02^{bC}	$0.09\pm0.009^{a,bA}$	670.5 ± 12.0^{aC}
300		6.42 ± 0.03^{bC}	0.07 ± 0.016^{bA}	4.77 ± 0.01^{bC}	0.10 ± 0.009^{aA}	497.8 ± 19.4^{bC}
450		6.45 ± 0.01^{bC}	$0.08\pm0.006^{a,bA}$	4.77 ± 0.05^{bC}	0.10 ± 0.011^{aA}	513.8 ± 12.9^{bC}
600		4.29 ± 0.01^{cC}	0.10 ± 0.003^{aB}	3.82 ± 0.01^{cC}	0.11 ± 0.005^{aB}	27.4 ± 0.7^{cB}
0.1	1:3	$7.35\pm0.01^{a,bB}$	0.08 ± 0.003^{aA}	5.66 ± 0.08^{aB}	0.03 ± 0.013^{cB}	1271.6 ± 71.3^{bB}
150		7.52 ± 0.01^{aB}	0.07 ± 0.004^{aA}	5.58 ± 0.04^{bB}	0.09 ± 0.002^{bA}	1585.2 ± 23.9^{aB}
300		7.08 ± 0.08^{cB}	0.08 ± 0.009^{aA}	5.63 ± 0.02^{aB}	$0.11\pm0.011^{a,bA}$	914.7 ± 99.5^{cB}
450		$7.25\pm0.07^{b,cB}$	0.07 ± 0.005^{aA}	$5.63\pm0.03^{a,bB}$	$0.11\pm0.008^{a,bA}$	$1134.7\pm98.5^{b,cB}$
600		5.22 ± 0.07^{dB}	0.09 ± 0.041^{aB}	4.66 ± 0.08^{cB}	0.12 ± 0.004^{aB}	79.8 ± 4.9^{dB}
0.1	1:2	8.80 ± 0.02^{aA}	0.06 ± 0.001^{cB}	$6.67\pm0.04^{a,bA}$	$0.06\pm0.007^{b,cA,B}$	5874.7 ± 120.2^{aA}
150		8.69 ± 0.03^{bA}	$0.07\pm0.001^{b,cA,B}$	$6.61\pm0.01^{b,cA}$	0.09 ± 0.005^{aA}	5187.8 ± 169.2^{bA}
300		8.61 ± 0.03^{cA}	$0.07\pm0.005^{a,bA}$	6.74 ± 0.06^{aA}	$0.08\pm0.016^{a,bA}$	4627.4 ± 194.9^{cA}
450		8.25 ± 0.01^{eA}	0.08 ± 0.004^{aA}	6.49 ± 0.02^{cA}	$0.07\pm0.006^{a,bB}$	3173.1 ± 27.7^{dA}
600		8.36 ± 0.01^{dA}	0.08 ± 0.002^{aB}	6.55 ± 0.03^{cA}	0.04 ± 0.008^{cC}	3560.0 ± 56.7^{dA}

Mean values (n = 6) ± SD.

[a-d]For each rheological parameter and for the same flour-to-water ratio, means without the same letter are significantly different ($P < 0.01$) according to the LSD multiple range test.

[A-D]For each rheological parameter and for the same high hydrostatic pressure treatment, means without the same letter are significantly different ($P < 0.01$) according to the LSD multiple range test.

$\ln G'_0$, $\ln G''_0$, n', and n'', regression coefficients relating G' or G'' and frequency (ω). $G'_0 - G''_0$, gel strength.

Table 4

Effect of high hydrostatic pressure treatment (at 25 °C for 15 min) and slurry concentration on pasting properties during non-isothermal heating (from 30 to 90 °C) of chickpea flour slurry.

High pressure (MPa)	Ratio (flour-to-water)	T_o (°C)	T_c (°C)	η^*_o (Pa s)	η^*_c (Pa s)	Viscosity breakdown (%)
0.1	1:5	72.7 ± 1.1^{bA}	90 ± 0.0^{aA}	0.017 ± 0.002^{bB}	11 ± 1.2^{aD}	-
150		74.2 ± 0.8^{aA}	90 ± 0.0^{aA}	0.017 ± 0.002^{bB}	11 ± 0.9^{aD}	-
300		73.1 ± 1.0^{bA}	90 ± 0.0^{aA}	0.017 ± 0.001^{bB}	7 ± 2.0^{bD}	-
450		72.3 ± 0.6^{bA}	90 ± 0.0^{aA}	0.017 ± 0.001^{bB}	0.3 ± 0.2^{cD}	-
600		60.3 ± 0.9^{cA}	90 ± 0.0^{aA}	0.021 ± 0.002^{aD}	0.3 ± 0.1^{cC}	-
0.1	1:4	66.4 ± 0.5^{bB}	90 ± 0.0^{aA}	0.017 ± 0.002^{bB}	444.6 ± 35.6^{cC}	-
150		68.0 ± 0.5^{aB}	90 ± 0.0^{aA}	0.017 ± 0.002^{bB}	1194 ± 180.6^{aC}	-
300		68.3 ± 0.9^{aB}	90 ± 0.0^{aA}	0.017 ± 0.003^{bB}	621 ± 34.8^{bC}	-
450		66.8 ± 0.4^{bC}	90 ± 0.0^{aA}	0.017 ± 0.001^{bB}	504 ± 22.9^{bC}	-
600		56.8 ± 1.1^{cB}	90 ± 0.0^{aA}	0.031 ± 0.001^{aC}	301 ± 19.7^{dB}	-
0.1	1:3	68.5 ± 0.3^{aB}	85.6 ± 1.2^{aB}	0.018 ± 0.002^{bB}	2463 ± 232^{aB}	1.9 ± 0.5^{dB}
150		67.3 ± 1.2^{bB}	83.5 ± 0.9^{bB}	0.019 ± 0.002^{bB}	2437 ± 165^{aB}	7.2 ± 1.4^{cB}
300		68.6 ± 0.8^{aB}	82.4 ± 1.4^{bB}	0.019 ± 0.003^{bB}	3154 ± 56^{bB}	11.3 ± 0.9^{bB}
450		69.1 ± 0.4^{aB}	83.5 ± 0.6^{bB}	0.019 ± 0.003^{bB}	3032 ± 122^{bB}	6.8 ± 1.1^{cB}
600		54.3 ± 1.2^{cB}	86.1 ± 0.3^{aB}	2 ± 0.9^{aB}	433 ± 35^{cB}	23.4 ± 3.5^{aA}
0.1	1:2	64.6 ± 0.7^{bC}	82.0 ± 0.8^{aC}	0.035 ± 0.012^{dA}	7736 ± 128^{bA}	7.7 ± 1.2^{dA}
150		66.6 ± 0.7^{bB}	78.9 ± 1.3^{bC}	0.068 ± 0.022^{cA}	7071 ± 54^{bA}	46.6 ± 4.6^{aA}
300		68.4 ± 1.1^{aB}	79.3 ± 1.4^{bC}	0.131 ± 0.014^{bA}	8640 ± 198^{aA}	48.5 ± 5.6^{aA}
450		64.7 ± 0.5^{bC}	79.9 ± 0.9^{bC}	0.151 ± 0.035^{bA}	8731 ± 110^{aA}	32.5 ± 2.9^{bA}
600		38.3 ± 1.0^{cC}	80.6 ± 1.1^{bC}	43 ± 4.4^{aA}	3824 ± 46^{cA}	17.8 ± 1.2^{cB}

Mean values (n = 6) ± SD.

$^{a-d}$For each parameter and for the same flour-to-water ratio, means without the same letter are significantly different (P < 0.01) according to the LSD multiple range test.

$^{A-D}$For each parameter and for the same high hydrostatic pressure treatment, means without the same letter are significantly different (P < 0.01) according to the LSD multiple range test.

T_o, onset temperature of gelatinization; T_c, conclusion temperature of gelatinization; η^*_o, complex viscosity at the beginning of the gelatinization process; η^*_c, complex viscosity at the end of the gelatinization process.

Highlights

- HHP treatment significantly increased the consistency of chickpea flour slurry.
- An increase in pressure level significantly decreased heat-induced paste strength.
- Pasting profiles show additional changes in viscosity occurring in later heating.
- Enthalpy of HHP-treated slurry showed gelatinization rising with pressure level.
- HHP-treated soft paste could be used to develop new chickpea-based products.